The Infrared Spectra of HOCl and DOCl

KENNETH HEDBERG AND RICHARD M. BADGER
Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California*
(Received February 16, 1951)

WE have recently observed the spectra of hydrogen hypochlorite and deuterium hypochlorite in the region 1–15μ as part of a general program of study of simple molecules. Since, so far as we are aware, no spectroscopic data has heretofore been reported on these substances, the preliminary results are of sufficient interest to be presented at this time.

The hypochlorites were prepared by mixing H_2O or D_2O vapor with Cl_2O gas in the absorption cell. The latter gas was prepared by the action of Cl_2 on HgO,[1] dried over $Mg(ClO_4)_2$, and fractionally distilled, a middle fraction being used for the experiments.

Low dispersion spectra were obtained with a Beckman IR-2 recording spectrophotometer (NaCl prism), and high dispersion spectra were obtained with a vacuum grating spectrometer.[2] The 42-cm absorption cell was equipped with NaCl windows cemented on with Apiezon W wax. Spectra were taken at several different partial pressures for each reactant; but, because of lack of knowledge concerning the extent of the gas phase reaction, the partial pressures of the resulting hypochlorites are not known.

Low dispersion spectrograms for HOCl and DOCl are shown in Fig. 1, and the bands observed are listed in Table I. The P branch of the band due to the ν_3 vibration (739 cm^{-1}) is in each case overlapped by a Cl_2O band. The first overtone of the O–H stretching mode ($2\nu_1$) of HOCl (Fig. 2) was studied under high dispersion and the coarse rotational structure resolved. This band is a nice example of a hybrid band of a nearly symmetrical top molecule with the top axis the least axis of inertia. Analysis of the band gave the results summarized in Table II. Only enough lines were observed to permit the determination of three values for $A''-\tilde{B}''$† and four for $A'-\tilde{B}'$, and unfortunately the positions of several of these lines are made uncertain by overlapping lines from the 1.4μ water band, leading to corresponding uncertainties in the rotational constant. If it is assumed that the best value for $A''-\tilde{B}''$ is about 19.97 cm^{-1} (obtained by a reasonable extrapolation) and that $\tilde{B}''$ is about 0.48 cm^{-1} (which may be calculated by adopting $r_{OH}=0.957$Å as in water,[3] $r_{OCl}=1.70$A as in chlorine monoxide,[4] and $\angle HOCl=90$–$120°$),‡ then $\angle HOCl$ is calculated to be about 113°.

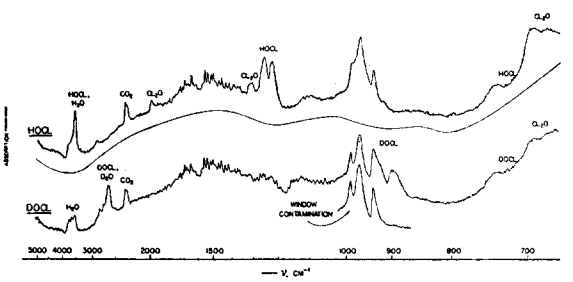

FIG. 1. Spectra of HOCl and DOCl. HOCl: $P_{Cl_2O}=410$ mm, $P_{H_2O}=7.7$ mm; DOCl: $P_{Cl_2O}=120$ mm, $P_{D_2O}=18.5$ mm.

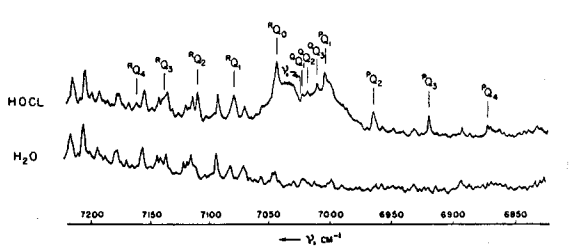

FIG. 2. The 1.42μ band ($2\nu_1$) of HOCl.

TABLE I. Observed and calculated vibrational frequencies for HOCl and DOCl, cm^{-1} (vac).

HOCl obs.	HOCl calc.	DOCl obs.	DOCl calc.	Assignments
739	742	739	733	ν_3 (O–Cl)
1242	1240	911	916	ν_2 (bend)
3626	3627	2674	2675	ν_1 (O–H)
7024	—	—	—	$2\nu_1$

TABLE II. Analysis of the 7023.9-cm^{-1} ($2\nu_1$) band of HOCl.

K	⊥ Component ^RQ, cm^{-1}	^PQ, cm^{-1}	$A''-\tilde{B}''$	$A'-\tilde{B}'$	∥ Component ^QQ, cm^{-1}	$\frac{(A'-A'')}{(\tilde{B}'-\tilde{B}'')}$
0	7043.2					
1	7078.0	7003.3	19.88	18.68	7022.0	1.90
2	7108.7	6963.7	19.85	18.12	7017.6	1.58
3	7137.4	6919.2	19.73	18.18	7009.7	1.58
4	7161.6	6871.9		18.11		

The fundamental vibrational frequencies shown in Table I were used to calculate values for the potential constants in the potential function

$$2V=k_{OH}\Delta r_{OH}^2+k_{OCl}\Delta r_{OCl}^2+k_\theta r_{OH}r_{OCl}\Delta\theta^2+2g r_{OCl}\cdot\Delta r_{OCl}\Delta\theta.$$

The calculation was carried out using the $F-G$ matrix method of Wilson,[5] assuming the above values for the structural parameters of the molecule. In order to obtain reasonable values for the potential constants, it was found necessary to factor off[6] the highest frequency for each molecule. The factored frequencies gave appreciably different values for the O–H, D stretching force constant, a k_{OH} and a k_{OD} (Table III). The k_{OH} and k_{OD} values were then substituted into the equations for HOCl and DOCl, respectively, which were solved for the remaining potential constants. This technique, which provides in effect a correction for the anharmonicities associated with the OH and OD stretching vibrations, yields the two sets of values for the constants k_{OCl}, k_θ, and g shown in Table III. Each set, together with the appropriate $k_{OH,OD}$ leads to the calculated frequencies shown in Table I.

TABLE III. Potential constants for HOCl and DOCl ×10^{-5} dynes/cm.

Constant	From HOCl	From DOCl	From both HOCl, DOCl Set 1	Set 2
$k_{OH,OD}$	7.35	7.54		
k_{OCl}			3.86	4.02
$k\theta$			$0.84_7\cdot r_{OH}^2$	$0.84_8\cdot r_{OH}^2$
g			$0.46_4\cdot r_{OH}$	$0.60_0\cdot r_{OH}$

The frequency product ratio for HOCl and DOCl predicted by the Teller-Redlich product rule differs from the observed by about 1.8 percent:

$$\nu_1^i\nu_2^i\nu_3^i/\nu_1\nu_2\nu_3=(mM^i/m^iM)(I_z^i/I_z)^{\frac{1}{2}}=0.531,$$
$$\nu_1^i\nu_2^i\nu_3^i/\nu_1\nu_2\nu_3=0.541,$$

where the superscript i refers to DOCl. This difference almost certainly arises chiefly from the anharmonicities associated with the OH and OD stretching vibrations. By multiplying the observed frequency ratio by $(k_{OH}/k_{OD})^{\frac{1}{2}}$, a quantity which should provide a good correction for the error introduced by the use of the observed instead of the zeroth order frequencies, one obtains the value 0.534, in much better agreement with the predicted value.

We intend to continue our study of HOCl and DOCl with the hope of obtaining improved experimental data to permit a more complete rotational analysis and the determination of a more complete potential function.

We are grateful to Professor Bryce L. Crawford for helpful discussions.

* Contribution No. 1528.

† $\tilde{B}=\frac{1}{2}(B+C)$.

‡ The *Pr* separation is ~30 cm^{-1}, from which the value $\tilde{B}=0.53$ is calculated [S. L. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933)].

[1] C. H. Secoy and G. H. Cady, J. Am. Chem. Soc. **62**, 1036 (1940).
[2] Badger, Zumwalt, and Giguére, Rev. Sci. Instr. **19**, 861 (1948).
[3] See G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, New York, 1945), p. 489.
[4] J. D. Dunitz and K. Hedberg, J. Am. Chem. Soc. **72**, 3108 (1950).
[5] E. Bright Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939).
[6] B. L. Crawford and S. R. Brinkley, Jr., J. Chem. Phys. **9**, 69 (1941).

The Infrared Spectra of Cl_2O and ClO_2

KENNETH HEDBERG
*Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California**

(Received February 16, 1951)

THE infrared spectra of Cl_2O[1] and of ClO_2[2a] in the 1–18 μ-region has been obtained by Bailey and Cassie. In the course of our study of HOCl and DOCl (preceding note), we have had occasion to re-examine the infrared spectrum of each of these substances in the 1–15 μ-region. The results of our work have revealed points of interest in connection with each compound: For Cl_2O, it seems certain that the band at 1245 cm^{-1} observed by Bailey and Cassie and designated as $\nu_2+\nu_3$ in the most plausible assignment[3] of the vibration of frequencies is actually to be attributed to the ν_2 (bending) vibration of HOCl (Fig. 1). For

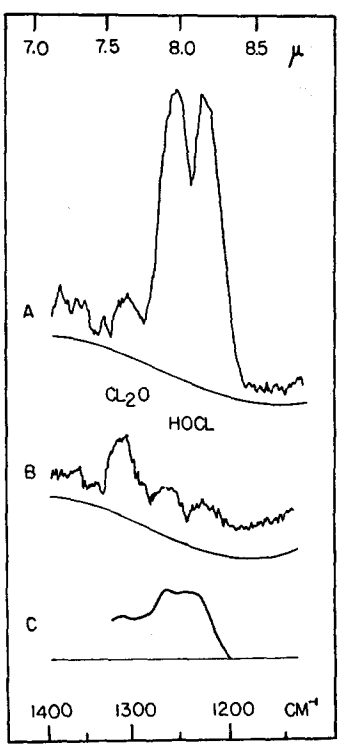

FIG. 1. Spectrum of Cl_2O and H_2O mixture. (A) $P_{Cl_2O}=410$ mm, $P_{H_2O}=15.0$ mm; (B) $P_{Cl_2O}=625$ mm, P_{H_2O} very small; (C) Representation of spectrum as observed by Bailey and Cassie (see reference 1) in this region.

ClO_2 we have observed two new bands which serve to substantiate the correctness of the early assignment.[2b]

The preparation of the Cl_2O and the apparatus used in the experiments is described in the preceding note. The ClO_2 was prepared after the description of Spinks and Taube,[4] and purification procedures similar to those employed with Cl_2O were followed.

In Fig. 1 are shown the spectrum of Cl_2O, Cl_2O+H_2O, and the curve obtained by Bailey and Cassie for Cl_2O. It is clear from the curves that the sample of Cl_2O used in these investigators' experiments was contaminated by HOCl (preceding note), probably present as a result of inadequate drying of their material. We have found that considerable care must be taken in the drying process in order to remove all water; evidence of the presence of HOCl is still seen in curve *B* even though the gas had been passed through a $Mg(ClO_4)_2$ drying tube. Since the spurious band of HOCl provided support for the location of ν_2 at ~320 cm^{-1}, the evidence for the frequency of this fundamental is somewhat weakened.

TABLE I. Vibrational frequencies for ClO_2.

Freq., cm^{-1}	Rel. intensity	Type	Assignment
3333	v.w.	—	$3\nu_3$
2954	w	—	$2\nu_1+\nu_3$
2031	m	—	$\nu_1+\nu_3$
1870	w	—	$2\nu_1$
1108	v.s.	∥	ν_3
945	s	⊥	ν_1

In Table I the bands observed for ClO_2 are shown. The new bands at 3333 cm^{-1} and 2954 cm^{-1} support the early assignment of ν_1 and ν_3. The $P-R$ branch separation in ν_1 is about 26 cm^{-1}, in rough agreement with the value 22 cm^{-1} calculated from the geometry of the molecule as determined by electron diffraction.[5]

We have calculated a number of values for the three potential constants, k, k_θ/r^2, and k_{12} for Cl_2O and ClO_2 from the dimensions and assumption of the general potential function,

$$2V=k_r[(\Delta r_1)^2+(\Delta r_2)^2]+k_\theta\Delta\theta^2+2k_{12}\Delta r_1\Delta r_2+2l(\Delta r_1+\Delta r_2)\Delta\theta,$$

using the fourth constant l/r as a parameter. A part of the results obtained is shown in Table II. The values of the bond stretching

TABLE II. Potential constants for Cl_2O and ClO_2, $\times10^{-5}$ dyne/cm.

Frequencies, cm^{-1} assign.	obs.	l/r (assumed)	k	k_θ/r^2	k_{12}
		Cl_2O			
ν_1	688	+0.0$_5$*	3.7	0.8	−1.2
ν_2	(320)[a]	+4.5*	5.7	2.0	+0.8
ν_3	969	+0.1 to +1.0	3.9 to 4.9$_5$	0.6$_5$ to 0.5	−1.0 to +0.1
		ClO_2			
ν_1	945	−1.4*	4.4	1.4	−1.6$_5$
ν_2	(447)[b]	+3.5*	6.1	2.0	−0.7$_5$
ν_3	1108	−1.0 to +1.0	6.1 to 7.1	0.6$_5$ to 0.7$_5$	−0.9 to +0.1

[a] See reference 3.
[b] See reference 2b.
* Limiting values which give real solutions for the other potential constants.

constants found by assuming that the interaction constants are small ($|k_{12}|$, $|l/r|\leqslant1.00$ as shown in last line of Table II for each molecule) are in accord with the idea that the bonds in ClO_2 are essentially double bonds.[5] We feel that the values for the other constants are not very reliable because of uncertainty in the frequency of the ν_2 vibration; however, this uncertainty does not affect the magnitudes of the bond stretching constants sufficiently to invalidate the conclusion reached as to the bond character.

* Contribution No. 1529.

[1] C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. (London) **142A**, 129 (1933).
[2a] C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. (London) **137A**, 622 (1932).
[2b] J. B. Coon, Phys. Rev. **58**, 926 (1940).
[3] G. B. B. M. Sutherland and W. G. Penny, Proc. Roy. Soc. (London) **156A**, 678 (1936).
[4] J. W. Spinks and H. Taube, Can. J. Research **B15**, 499 (1937).
[5] J. D. Dunitz and K. Hedberg, J. Am. Chem. Soc. **72**, 3108 (1950).

Thermal Diffusion in Hydrogen-Water Vapor Mixtures

E. WHALLEY
Division of Chemistry, National Research Council, Ottawa, Canada

(Received February 15, 1951)

THERMAL diffusion in hydrogen-water vapor mixtures has been studied by Shibata and Kitagawa.[1] They have calculated the thermal diffusion ratio k_T from the slope of their